

## A SEARCH FOR THE RADICAL HYDROGEN TRANSFER PATHWAY IN COAL HYDROLIQUEFACTION.\*

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### INTRODUCTION

It is generally accepted that the formation of petroleum liquids produced in the thermal liquefaction of coal can not be completely explained by simple homolytic cleavage of strong linkages in coal structures. Model compound studies have been employed to elucidate the mechanisms of scission of strong bonds in coal structures and have provided useful information for increasing the efficiency of the coal liquefaction processes (1).

Radical Hydrogen Transfer (RHT), the transfer of a hydrogen atom from a solvent-derived cyclohexadienyl substituted radical to the ipso position of an aryl-alkyl linkage, has been proposed as an important pathway for the cleavage of strong bonds in coal structures during coal liquefaction (2-4). Elegant numerical modeling studies of the scission of diarylmethane model compounds in the presence of a variety of solvent molecules demonstrated that an alternative mechanism for the scission of the strong bonds in these model compounds may be operative that involves cyclohexadienyl-derived solvent molecules rather than free hydrogen atoms. These studies predicted an activation barrier of 18 to 22 kcal/mol for an endothermic transfer of a hydrogen atom from a cyclohexadienyl solvent molecule to the ipso position of a diarylmethane model compound (5-7). Furthermore, these studies have been utilized to predict the efficiencies of hydrogen donor solvents in the liquefaction of coal samples (8,9). The evidence, however, does not preclude other mechanisms involving the cyclohexadienyl solvent molecules. Other possible mechanisms include an addition-transfer-elimination reaction (10) or other, more traditional radical mechanisms that do not require an exotic reaction pathway involving a hydrogen atom carrier donating a hydrogen atom to a closed shell species.

### EXPERIMENTAL

The model compound, 3,6-dihydro-3-methoxycarbonyl bibenzyl, 2, was prepared by the following reaction sequence. *m*-bromobenzaldehyde was added to an ether solution of benzyl grignard at room temperature to yield the expected alcohol. The alcohol was converted to the chloride ( $\text{SOCl}_2$ ) and reduced with  $\text{LiAlH}_4$  to give *m*-bromobibenzyl. A grignard reagent from *m*-bromobibenzyl was quenched with  $\text{CO}_2$ . Following acidic work-up esterification in methanol gave the methyl ester. Birch reduction of the ester yielded our model compound, 2.

Decane solutions of the ester, 2, ( $10^{-3}$  M to  $10^{-4}$  M) containing an internal standard for GC product analysis were prepared in quartz tubes. The

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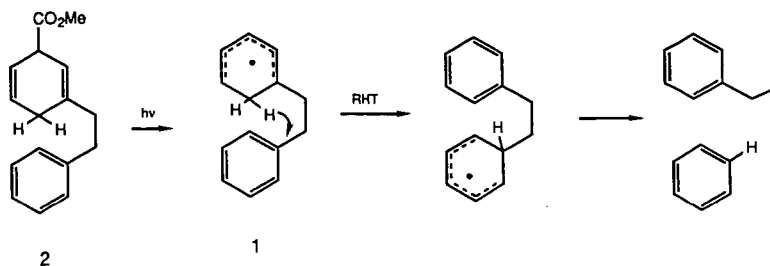
samples were degassed, using three freeze-thaw cycles, and sealed under vacuum. The sealed tubes were irradiated with a high-pressure, 1000-W Hg lamp through the quartz window of a hot air bath, and the temperature was monitored using a thermocouple. Photolysis times ranged from 10 to 15 minutes to yield about 30% decomposition of the starting material. Control experiments showed that the ester was thermally stable under the reaction conditions. Products were analyzed on a HP 5890A GC using on-column injection techniques and were identified by the retention times and GC/mass spectra of authentic compounds.

## RESULTS AND DISCUSSION

Our approach to this problem was to design and prepare a new model compound that would provide an unambiguous answer to our question, "What role does Radical Hydrogen Transfer play in the cleavage of strong bonds in coal liquefaction?" We chose a model compound that would provide us with a cyclohexadienyl radical hydrogen donor and an alkyl-phenyl hydrogen acceptor within the same molecule. We anticipated several advantages to this approach in the preparation of our model compound 3,6-dihydro-3-methoxycarbonyl bibenzyl, **2**:

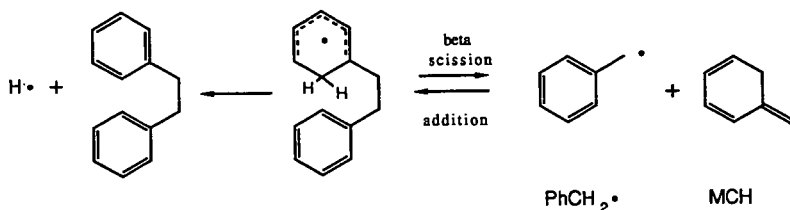
- 1) The cyclohexadienyl transferring agent could conveniently be prepared from a Norrish Type I photo-cleavage of the methyl ester, **1**, at any desirable temperature and at very low rates of initiation favoring unimolecular RHT or scission reactions over bimolecular termination;
- 2) A thermal-neutral hydrogen transfer from a cyclohexadienyl to a phenyl aromatic would provide a lower activation barrier than the endothermic barrier from the numerical modeling studies;
- 3) An intramolecular hydrogen transfer would increase the Arrhenius factor ( $\log A$ ) from 8.5 (bimolecular RHT) to 10 to 11 (intramolecular RHT) thereby suppressing competing side reactions;
- 4) Intramolecular RHT of **1** would proceed through a transition structure of nearly optimal regio- and stereo-chemical orientation, a 1,5 hydrogen migration (11) to yield benzene and phenylethyl radical products as shown in Scheme I;

Scheme I



- 5) A competing  $\beta$ -scission reaction of the cyclohexadienyl radical 1 to yield benzyl radical and methylenecyclohexadiene (MCH) products would provide an internal "clock" to quantify the activation barrier for RHT in this model system as shown in Scheme II;

Scheme II



Irradiation of a dodecane solution containing the methyl ester, 2, ( $2.4 \times 10^{-4}$  M) heated to  $250^\circ C$  in a quartz reactor vessel led to the decomposition of the model compound and the appearance of two cleavage products, toluene (8%) and bibenzyl (24%), yields are based on conversion of starting material. Control experiments showed that the methyl ester was thermally stable under the reaction conditions. Benzene, the RHT product, was not detected.

Irradiation of a concentrated solution of 2 ( $1.6 \times 10^{-3}$  M) under the above reaction conditions gave the same products, toluene (3%) and bibenzyl (18%) but no benzene. The decrease in yield of toluene was expected because higher concentrations of benzyl radical lead to an increased rate of termination.

These results require that RHT from the cyclohexadienyl radical to the appended phenyl ring not compete with  $\beta$ -scission of the cyclohexadienyl radical in this model compound,  $E_a$  (RHT)  $>$   $E_a$  ( $\beta$ -scission). Although we did not observe RHT products in this model system, a lower limit for the activation barrier of a RHT pathway for this system can be determined. This lower limit can be obtained from a calculation of activation barrier for the competing  $\beta$ -scission reaction (Scheme II) determined by Equation [1].

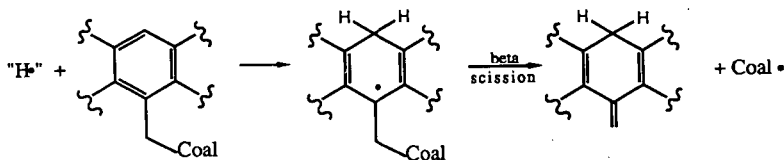
$$E_a = \Delta H_f^\circ(\text{MCH}) + \Delta H_f^\circ(\text{PhCH}_2^\bullet) + E_a(\text{addition}) - \Delta H_f^\circ(1) \quad [1]$$

Only one approximation is necessary in our calculation: The barrier for addition of benzyl radical to methylenecyclohexadiene (MCH), which is the reverse reaction of  $\beta$ -scission. The addition of benzyl radical to styrene was determined to have a barrier of 7 kcal/mol (12). We assume that the barrier for the more exothermic reaction, addition of benzyl radical to MCH, will be no less than 4 kcal/mol. The thermochemical data for the products of the  $\beta$ -scission reaction

were determined previously. We used 48 kcal/mol as the  $\Delta H_f^\circ$  of benzyl radical (13), and 35 kcal/mol as the  $\Delta H_f^\circ$  of MCH (14) and we calculated the  $\Delta H_f^\circ$  of radical 1 to be 60.6 kcal/mol (15). The solution to Equation [1] yields a barrier of  $28 \pm 3$  kcal/mol for  $\beta$ -scission of cyclohexadienyl radical 1 to yield MCH and benzyl radical, just slightly lower than the barrier we calculate for scission of hydrogen atom from a cyclohexadienyl radical ( $E_a = 30$  kcal/mol).

It is important to note that this novel  $\beta$ -scission reaction can be responsible for the cleavage of "strong bonds" in coal structures at relatively low temperatures if the appropriate hydrogen atom donors are available. Our new finding suggests that addition of hydrogen atoms to non-ipso ring positions should promote bond cleavage by this  $\beta$ -scission pathway as shown in Scheme III. In this

Scheme III



work  $\beta$ -scission just barely competes with loss of hydrogen ( $E_a = 30$  kcal/mol). However, with the addition of hydrogen atoms to larger ring systems the  $\beta$ -scission reaction becomes more important because the barrier for hydrogen loss increases with increasing ring size. When the alkyl linkages are longer than two carbon units the barrier of scission increases, obviously the stability of the radicals produced is a driving force, but  $\beta$ -scission may still compete with loss of hydrogen in larger ring systems. The barrier for  $\beta$ -scission of diarylmethanes is prohibitively high, due to the formation of aryl radicals, and therefore would not have been observed in the numerical model studies.

#### CONCLUSION

Our examination of the RHT process yields an important result. Our model compound allowed us to "isolate" the RHT process from any competing intermolecular cleavage reaction involving cyclohexadienyl solvent molecules. Our 6-(2-phenyl-ethyl)-cyclohexa-1,3-dien-6-yl radical is consumed by a  $\beta$ -scission pathway, with an activation barrier we calculate to be 28 kcal/mol. No RHT products are observed in our model system. This requires the  $E_a$  for RHT to be  $> 28$  kcal/mol, which is substantially higher than the value obtained by the numerical modeling studies ( $E_a$  16 to 22 kcal/mol).

There is convincing evidence that donor solvent structures play an active role, perhaps a predominant role in the cleavage of strong bonds (7-10). In the present work we have conveniently suppressed all side reactions from our

experiments in order to selectively examine the RHT contribution. We do not imply that a RHT pathway does not occur to some extent in the liquefaction of coal, we expect it to have a lower activation barrier than the well-documented Molecular Assisted Homolysis (MAH) reaction (17,18). However, unless significant tunneling of the hydrogen atom through the high barrier ( $>28$  kcal/mol) for RHT occurs, a low activation process responsible for the cleavage of strong bonds in coal structures must occur by an alternative mechanism. The addition-transfer-elimination mechanism (10), a concerted-transfer with elimination pathway (19), and a simple addition-abstraction-elimination reaction pathway are presently being investigated by this group.

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